X-RAY FLUORESCENCE ANALYSIS OF WHOLE COAL

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Introduction

Recent interest in the trace element content of coal has led to the need for development of rapid, accurate analytical methods for their determination. Because X-ray fluorescence analysis has demonstrated its usefulness in the determination of major, minor, and trace elements in numerous types of materials, it was felt that this method could be extended to trace element determinations in whole coal. In the past such analyses have been seriously hampered by the lack of standard samples. However, U. S. Environmental Protection Agency sponsored research, which is being conducted in our laboratories, has generated a large number of coal samples for which trace elements have been determined by two or more independent analytical procedures (viz. optical emission, neutron activation, atomic absorption and wet chemical methods). Using these coals as standards, a X-ray fluorescence method has been developed for the determination of a number of trace and minor elements in pressed whole coal samples.

The instrument used in this project was a Phillips manual vacuum X-ray fluorescence spectrometer. All analyses for this study were made in the Analytical Chemistry Laboratories of the Illinois State Geological Survey. The work upon which this report is based was partially supported by U. S. Environmental Protection Agency Contract 68-02-0246.

Preliminary Investigation of Major and Minor Elements in Whole Coal and Coal Ash

Two different types of materials - coal ash and whole coal - were analyzed in this project, and sample preparation was varied accordingly.

Whole coal was ground with 10 per cent by weight of a binder and pressed into a disc, which was used as the analytical sample without further treatment. Sample preparation techniques are given in detail in Illinois State Geological Survey Environmental Geology Note 61.

It was found that two grams of coal gave a disc that was infinitely thick with respect to soft X-rays emitted by "light" elements such as Mg, Si, Al, and Ca; however, for elements "heavier" than Br, it was necessary to increase the sample weight to attain infinite sample thickness, i.e., no X-rays penetrated through the pressed coal sample.

Our use of X-ray fluorescence was originally intended for the purpose of establishing major element matrix information on coal ashes to be analyzed for trace elements by optical emission spectroscopy. Both low temperature (<150° C) and high temperature (450° C) coal ashes, prepared as described by Ruch, Gluskoter, and Shimp (1973), were used for this purpose, and the method of Rose, Adler and Flannigan (1961) was adapted for the determination of major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, and V). The instrumental parameters used for these elements are given in Table 1. To assess the validity of this procedure, a series of analyzed coal ashes obtained from the British Coal Utilization Research Association (BCURA) were analyzed along with the two types of ash prepared in our laboratories. Calibrations for these analyses were prepared from National Bureau of Standards rock standards (1B, G1, W1, No. 78, No. 79, No. 88). The values determined for the BCURA coal ashes were in excellent agreement with published results of Dixon, Edwards, Flint, and James (1964). Standard deviations were calculated for duplicate coal ash determinations. They were: Si - .0715%, Ti - .0066%, Al - .0567%, Fe - .0493%, Mg - .0178%, Ca - .0282%, K - .0123%, P - .0074%, and V - 1.3 ppm. These deviations are comparable to "Class A" wet silicate analyses and are indicative of a high degree of accuracy.

Because of these encouraging results and previous work on brown coals by Sweatman, Norrish, and Durie (1963) and Kiss (1966), which indicated that major and

minor elements could be determined in <u>whole</u> coal, a series of 25 coals were prepared for analysis. For each coal, a low temperature ash, a high temperature ash and the whole coal itself were prepared for X-ray fluorescence analysis sample preparation procedures. When all values were converted to the whole coal basis, the agreement among the three types of coal materials was excellent (Table 2) indicating that the simpler and more rapid whole coal technique is acceptable for the determination of major and minor elements.

Determination of Trace Elements in Whole Coal

Trace element determinations on whole coal have been severely handicapped by the lack of analyzed standards. Because of this it has been necessary to prepare calibration curves from samples analyzed in our laboratories by other independent methods. The accuracy of the X-ray fluorescence method is, therefore, limited by the accuracy of the methods used for obtaining the trace element concentrations that were employed in preparing the calibrations. The difficulties encountered in uniformly adding known quantities of trace elements to ground whole coal prohibited the preparation of calibrations in that fashion.

The "light" coal matrix of carbon, hydrogen and oxygen and the relatively small variation of "heavier" trace elements permits their determination with a minimum of interferences. Using the same whole coal procedures as previously described for the determination of major and minor elements, P, V, Cr, Mn, Co, Ni, Cu, Zn, As, Br, Mo, and Pb have been determined directly in 50 whole coals.

The relative errors for all* elements determined are given in Table 4. These data indicate the precision obtained for the X-ray fluorescence analysis on duplicates of 15 samples of whole coal ground to -325 mesh. Accuracy of the X-ray fluorescence method was evaluated by calculating, from the 50 whole coals analyzed, the mean variation of each element* from its mean concentration as determined by the other independent methods previously mentioned (Table 5). Detection limits (three standard deviations above background) for each element are also given in Table 5.

X-Ray Matrix Corrections for Analysis of Whole Coal

Due to the lack of standards, variations in analyses made by other methods, and errors caused by coal sampling problems; it has been difficult to evaluate the need for X-ray matrix corrections and to select the best method for applying them. However, corrections were necessary because some elements in whole coal such as Fe, Si, and S may vary considerably. For these elements, corrections were applied indiscriminantly to all samples because it was impossible to determine the point at which matrix variations required a correction greater than the accuracy limits of the method. We elected to use the minimum number of corrections compatible with reasonably accurate results. As a result the elements Mg, Al, Si, P, S, Cl, K, and Mo were left uncorrected. While these determinations probably could be improved (Berman and Ergun, 1968) they were shown to be adequate for our purposes (Table 2). The Ti and V values were corrected by using the variations in whole coal iron content.

The method of correcting the other elements for matrix variations was that of Sweatman, Norrish and Durie (1963). A total mass absorption was determined by measuring the attenuation of the radiation in question by a thin layer of the sample to be analyzed. The mass absorption coefficient M was calculated by $M = \frac{A}{W} \ln \frac{Cs}{Cx}$;

where A = area of sample (cm^2); W = weight of sample in grams; Cs = intensity in counts per second of the standard; and Cx = intensity in counts per second of the standard attenuated by the coal sample. Using these coefficients, a corrected value was obtained for the elements determined even when matrix variations were considerable. It should be noted that great care was taken to press the coals to a uniform thickness so that the mass absorption coefficient was affected only by density (for which compensation was made) and matrix considerations.

* For completeness, whole coal minor element data are also included in the trace element tables.

Effect of Coal Particle Size Upon Trace Element Analytical Precision

Our results indicated that coals ground to -60 mesh did not yield a consistently acceptable precision for most trace element determinations. Therefore, it was necessary to evaluate the errors associated with the determination of trace elements in coals ground to different particle sizes.

Nine coals, representing a range of trace element concentrations, were carefully ground to pass screens of various mesh sizes (Table 6). Duplicate two gram coal samples for each mesh size were weighed and, then, all were further reduced in size by grinding for 3 minutes in a No. 6 Wig-L-Bug. The final grinding of analysis samples eliminated, as nearly as possible, any variation in the pressed coal discs, which were subsequently prepared for analysis according to Ruch, Gluskoter, and Shimp (1973). In all, over 1000 individual determinations were made in this study.

Table 6 gives the combined means of the differences between duplicate trace element determinations for each coal particle size analyzed. Both the means of the absolute differences (ppm) and the means of the relative differences (absolute difference expressed as a percentage of the concentration) are given. The results show that there is a progressive improvement in precision with decreasing coal particle size.

The ranges of relative differences between duplicate analyses for a number of trace elements at three coal mesh sizes are given in Table 3. With the exception of Br, the ranges are narrower for the -200 and -325 mesh sizes than they are for the -60 mesh coal.

Progressive reduction in coal particle size from -60 to -400 mesh resulted in the improvement of precision for all elements except Br. The combined mean for all elements was reduced below 5% for coal ground to pass a -200 mesh sieve.

These data indicate that for most purposes acceptable precision can be obtained on -200 mesh coal. Further improvement is achieved on grinding to -325 mesh, but this will usually be unnecessary except for analyses to be used as standard values or other special purposes. Variations in the original field sampling of coal would probably negate any improvements in precision that might be gained from grinding below the -325 mesh size.

While this study applied directly to X-ray fluorescence analysis of whole coal, it is felt that it should also apply to any method in which a limited sample (~ 3 grams or less) is taken for analysis.

Discussion and Conclusions

Good agreement of whole coal results, as determined by X-ray fluorescence, was obtained with those values determined by several other independent methods (Table 5). Some variations among the methods were found to occur at the higher trace element concentrations, especially for the more coarsely ground coals. Because this was true not only of the X-ray fluorescence method, but also of the other methods investigated, it was felt that the variations were due to sampling errors caused by the occurrence of discrete mineral particles such as pyrite and sphalerite in whole coal. This has now been demonstrated to be true by geologists at the Illinois State Geological Survey using the scanning electron microscope.

It is apparent from Table 5 that trace elements determined by the X-ray fluorescence method described in this report are limited to those elements occurring in whole coals at concentrations of a few parts per million or greater. Elements such as Se, Hg, and Sb, which are usually present in whole coal at levels below one ppm, are not capable of being determined by this method.

Our results indicate that X-ray fluorescence provides a highly useful tool for rapid and reasonably accurate analysis of whole coal for trace elements. Because of the speed and simplicity of the method, it is highly adaptable to large scale surveys of coal resources. While the limitations of this simple procedure may preclude the determination of certain elements, the time-saving factor over other methods (40 or 50 to 1 in the case of Br by neutron activation) without loss of accuracy may well make X-ray fluorescence the method of choice for many elements. The availability of improved equipment, such as nondispersive systems and automation, could extend the application of X-ray analysis to a dominate position for the determination of trace elements in whole coal.

TABLE 1 – SPECTROMETER PARAMETERS

Element	X-Ray	2 θ Angle	Background 2 θ	Crystal	X-Ray Tube	PHA Volts Base	PHA Volts Window
Si	KL_3 & KL_2	108.01°	111.01°	EDDT	Cr	7	17
Al	KL_3 & KL_2	142.42	145.95	EDDT	Cr	5	17
Ti	KL_3 & KL_2	86.12	89.12	LiF	Cr	5	18
Fe	KL_3 & KL_2	57.51	60.51	LiF	Cr	5	25
Ca	KL_3	44.85	47.95	EDDT	Cr	14	30
K	KL_3 & KL^2	50.32	53.90	EDDT	Cr	14	21
Mg	KL_{23}	136.69	139.69	ADP	Cr	4	8
V	KL_3 & KL_2	76.93	80.93	LiF	Cr	5	16
S	KL_3 & KL_2	75.24	78.38	EDDT	Cr	12	18
Cl	KL_3	64.94	67.94	EDDT	Cr	11	19
P	KL_3 & KL_2	110.99	113.99	Ge	Cr	9	15
Ni	KL_3 & KL_2	48.66	50.36	LiF	Cr	10	27
Cu	KL_3 & KL_2	45.02	49.67	LiF	Cr	11	28
Zn	KL_3 & KL_2	41.79	44.25	LiF	Cr	10	22
Pb	L_3N_5 & L_2M_4	28.24	31.24	LiF	Cr	22	28
Br	KL_3 & KL_2	29.97	35.12	LiF	Cr	25	23
As	KL_3 & KL_2	34.00	37.00	LiF	Cr	24	23
Co	KL_3 & KL_2	52.79	53.79	LiF	W	13	16
Mn	KL_3 & KL_2	62.97	63.97	LiF	W	8	12
Mo	KL_3 & KL_2	20.33	19.83 20.83	LiF	W	36	40
Cr	KL_3 & KL_2	69.35	68.35	LiF	W	7	15

TABLE 2 – MEAN ABSOLUTE VARIATION BETWEEN RAW COAL AND ASH

Element	(%) Average Difference	(%) Maximum Difference
Si	.10	.24
Al	.08	.12
Ti	.012	.030
Fe	.10	.17
Ca	.04	.12
K	.02	.04
P	.002	.005
Mg	.010	.015

TABLE 3 – RANGE OF RELATIVE ERRORS IN PERCENT AT THREE WHOLE COAL PARTICLE SIZES

Element	-60 Mesh	-200 Mesh	-325 Mesh
V	0.0 – 10.0	.3 – 5.0	.3 – 4.0
P	2.0 – 18.0	2.0 – 10.0	1.5 – 7.5
Ni	1.5 – 25.0	.0 – 20.0	1.5 – 8.0
Cu	.8 – 20.0	.2 – 1.0	.2 – 1.0
Zn	1.2 – 25.0	1.2 – 12.0	.1 – 6.5
Pb	.4 – 23.0	1.2 – 9.5	.4 – 5.0
As	.1 – 6.0	.1 – 4.0	0.0 – 1.5
Br	0.0 – 4.0	0.0 – 3.5	0.0 – 3.0

TABLE 4 – DEVIATIONS ON –325 M WHOLE COAL		
Element	Standard Deviation	Relative Deviation (%)
	per cent	
Al	.021794	1.77
Si	.05319	1.96
S	.013038	.532
Cl	.0035496	1.13
K	.00370135	2.26
Ca	.005291	1.65
Mg	.002097	3.88
Fe	.021977	1.26
	ppm	
Ti	4.1580	.564
V	1.5801	3.84
Ni	1.11744	4.29
Cu	.74833	3.92
Zn	3.6105	1.37
As	.94291	2.49
Pb	1.5286	2.29
Br	.39o47	2.11
P	3.4066	10.92
Co	.4300	4.79
Mn	4.1429	7.53
Cr	1.1402	4.35
Mo	3.1080	23.9

TABLE 5 – COMPARATIVE ACCURACY FOR WHOLE COAL AND LIMITS OF DETECTION		
Element	Accuracy	Limit of Detection
	per cent	per cent
Al	± .08	.012
Si	± .10	.016
S	± .04	.003
Cl	± .01	.0015
K	± .02	.003
Ca	± .04	.0005
Mg	± .010	.015
Fe	± .10	.005
	ppm	
Zi	± 6.3	7.5 ppm
V	± 3.1	2.5 ppm
Ni	± 1.9	3.5 ppm
Cu	± 2.5	1 ppm
Zn	± 23.	2 ppm
As	± 4.3	3.2 ppm
Pb	± 7.7	1.8
Br	± 1.0	.5
P	± 15.	15 ppm
Co	± 1.3	2.5
Mn	± 3.4	4.5
Cr	± 2.1	1.5 ppm
Mo	± 5.2	5 ppm

TABLE 6 – MEAN ERROR FOR ALL ELEMENTS AT VARIOUS COAL PARTICLE SIZES		
Mesh size	ppm	(%) Error of Mean Element Concentration
–60 M	± 3.05	8.47
–100 M	± 2.11	6.38
–200 M	± 1.26	4.28
–325 M	± 1.12	2.62
–400 M	± 1.02	1.56
<<400 M	± .93	1.40

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